

(21) Application No: 0213690.1

(22) Date of Filing: 14.06.2002

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(51) INT CL<sup>7</sup>:  
**C04B 28/00**

(52) UK CL (Edition V):  
**C1H HCH H620 H717 H739 H742**

(56) Documents Cited:  
**WO 2001/070646 A1**      **WO 1997/049644 A1**  
**US 6332921 B1**      **US 5158613 A**  
**US 4935060 A**      **US 4877452 A**

(58) Field of Search:  
UK CL (Edition T) **C1H HCH**  
INT CL<sup>7</sup> **C04B**  
Other: Online: **WPI, EPODOC, PAJ**

(54) Abstract Title: **High temperature cement compositions for use downhole**

(57) In a process to design high temperature cement slurries, temperature stable mineral phases (such as anorthite and wairakite) are selected that will form at the downhole temperature of the well. Aluminium modifiers and silica oxides are added to the dry cement so that the elemental composition of the blend corresponds to the mineral phases selected. The control of the particle size distribution and the relative amount of those minerals allow their addition at high concentration while leaving the slurry easily mixable and pumpable. The kinetics that affect how quickly the thermodynamic equilibrium of the targeted mineral phases formation is reached, can be influenced by adjusting the crystallinity and the particle sizes of the different solids.

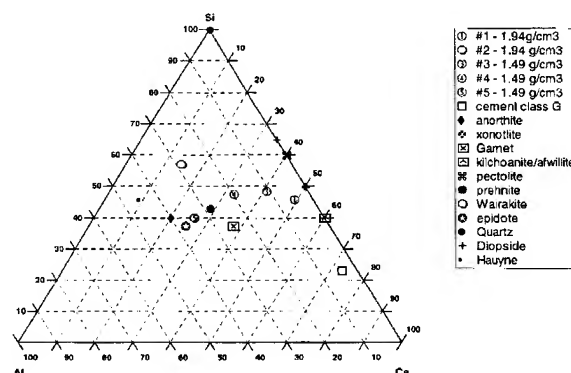


Figure 2

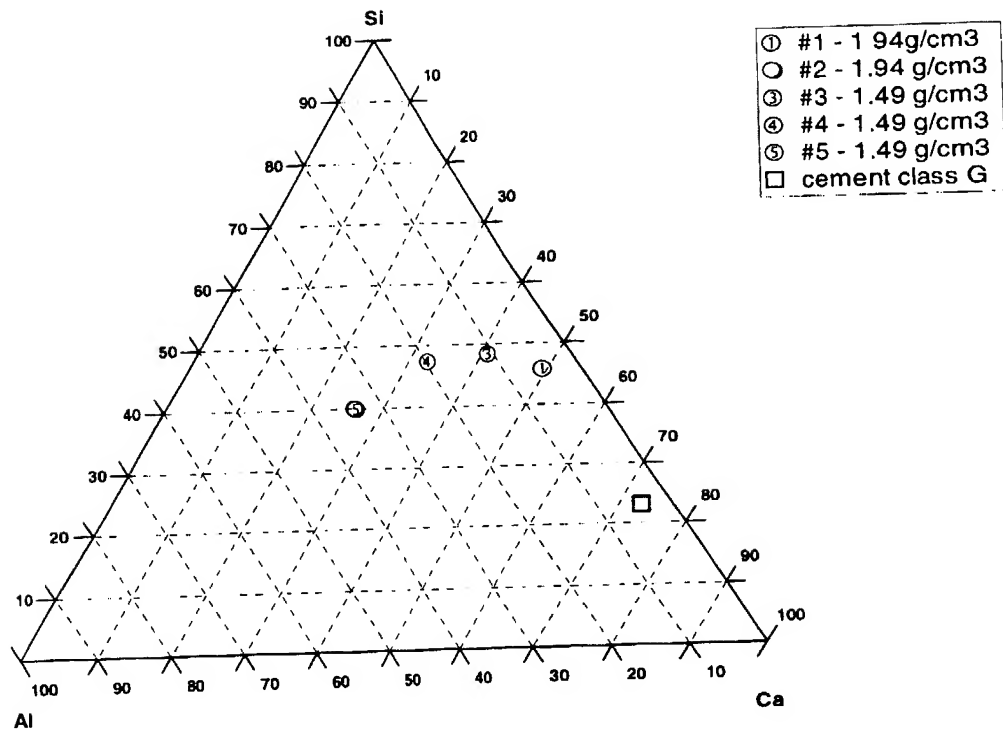


Figure 1

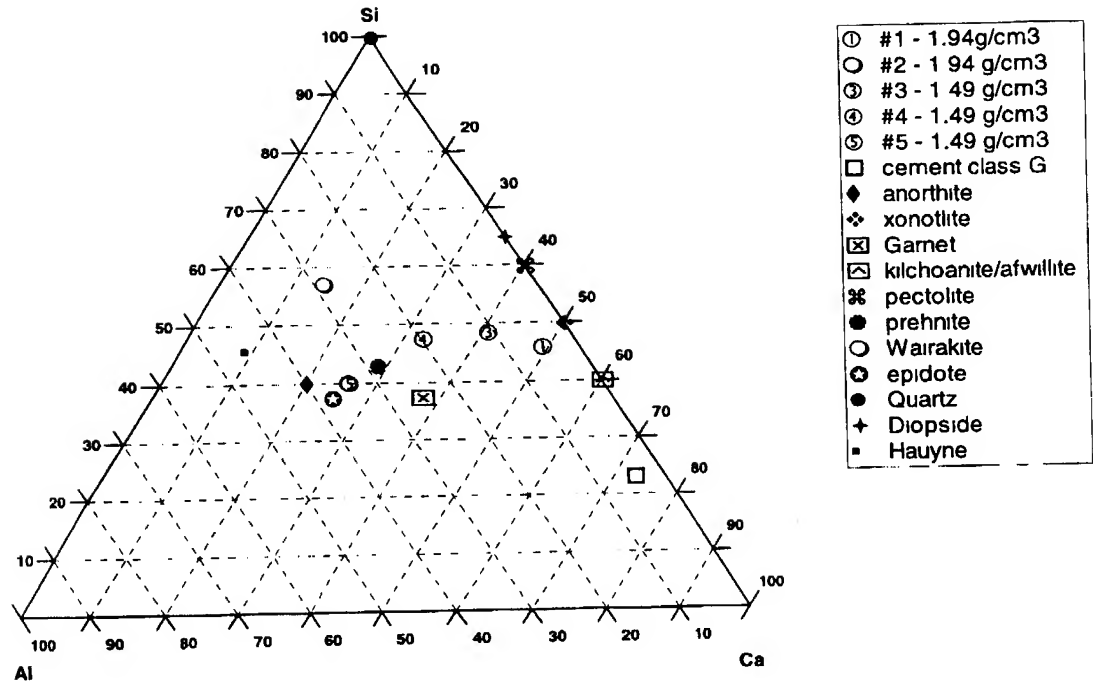
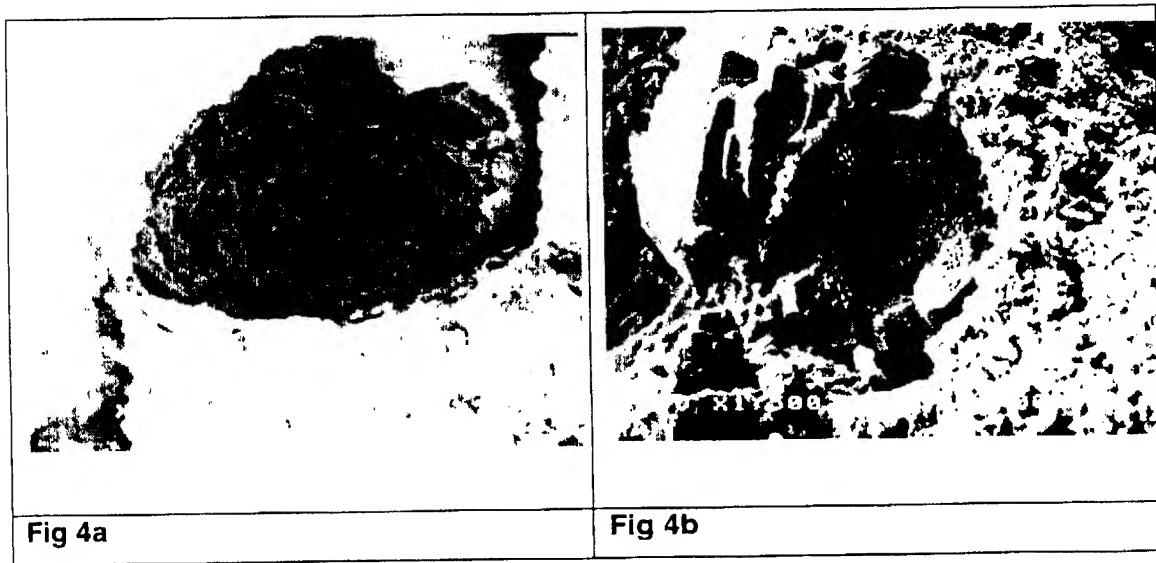
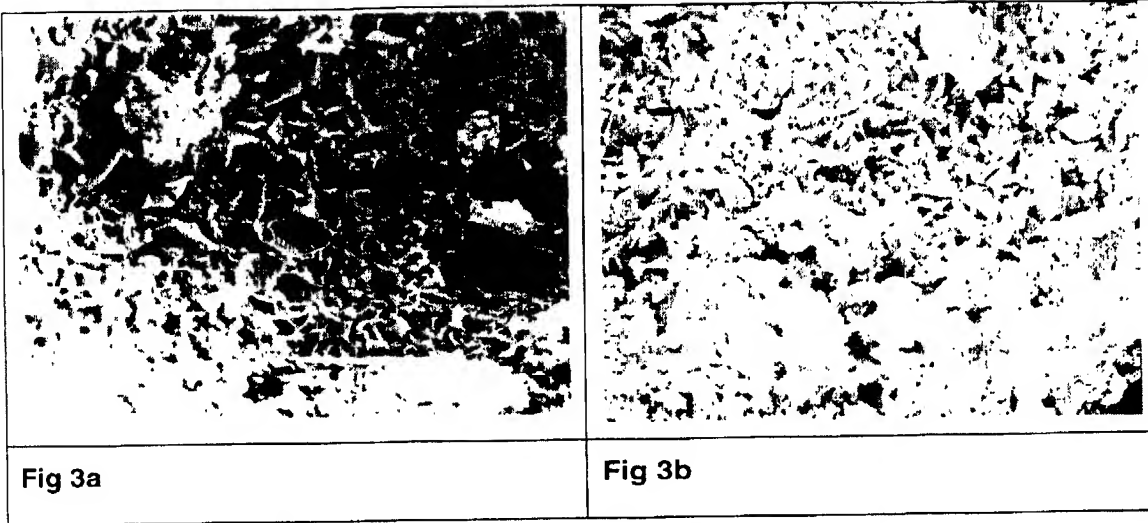
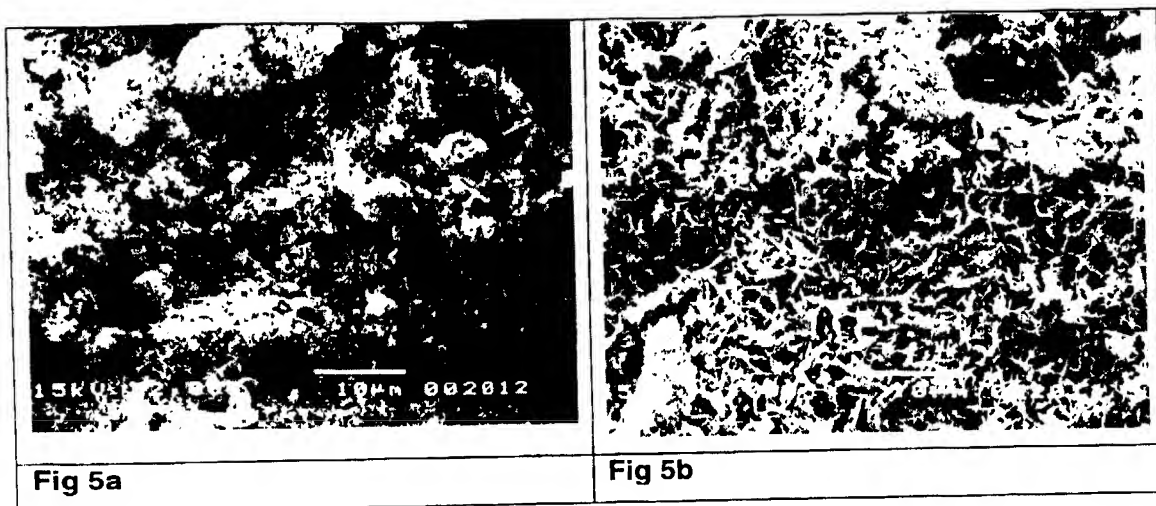


Figure 2





## HIGH TEMPERATURE CEMENT COMPOSITIONS

The present invention relates to compositions and methods for cementing operations conducted at high temperatures. In particular, the invention provides methods for designing slurries for use in cementing high-temperature wells such as geothermal wells or oil and gas wells.

After drilling an oil well or the like, a casing or coiled tubing is lowered into the hole and cemented over all or part of its depth. In particular, cementing prevents exchange of fluids between the different layers of formation traversed by the hole, prevents gas from rising in the annular space surrounding the casing or limits the ingress of water into the production well. Its principal purpose, of course, is to support the casing.

In the exploitation of geothermal wells or very high temperature oil and gas wells, environmental conditions are much severe than in normal oil wells, with very high temperatures and highly aggressive brine. For safety and others reasons, the set cement sheath has to be durable in order to keep its integrity and to protect the casing from corrosion and isolate the fluids present in the different geological formations (Berra, M. et al,(1988) Behaviour of a cementing hydraulic binder under severe geothermal conditions. Geothermics, Vol. 17, No. 5/6, pp 785-813).

In the vast majority of well cementing cases, a Portland cement is used as the hydraulic binder, a material that is composed of calcium silicates and calcium aluminosilicates. In the presence of water, those mineral phases hydrate and form hydrated calcium silicate (CSH) and also portlandite ( $\text{Ca(OH)}_2$ ) and aluminium sulphate. At temperatures below about  $100^\circ\text{C}$ , CSH is a gel, and is largely responsible for the cohesion and mechanical strength of the set cement in the short to medium term.

When the temperature exceeds about  $100^\circ\text{C}$ , in the first days or months the majority of cements lose compressive strength and become permeable. Then they regain their strength and their permeability reduces. That phenomenon, known as retrogression, is due to metamorphosis of CSH gel to a highly crystalline phase known as alpha

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dicalcium silicate,  $\alpha$ -C<sub>2</sub>SH, which is much more dense than CSH with a contraction in volume and an increase in the porosity of the cement. This results in disintegration of the cement, which increases in rate as the porosity increases, rendering it more sensitive to chemical attack such as channelling of brine or circulation of carbon  
5 dioxide.

To avoid the phenomenon of retrogression, it has been proposed to add silica in the form of sand or silica flour to compositions which have to withstand temperatures of more than 100°C. Adding 35% to 40% of silica (with respect to the weight of the  
10 Portland cement) brings the CaO/SiO<sub>2</sub> ratio (usually denoted C/S) to about 1.

With this modified composition, CSH gel reacts with the added silica to form the mineral tobermorite (C<sub>5</sub>S<sub>6</sub>H<sub>5</sub>) at about 110°C. When the temperature is raised to 150°C, the tobermorite transforms into xonotlite  
15 (C<sub>6</sub>S<sub>6</sub>H). These phases improve the stability and mechanical integrity of the cement at high temperatures; however, owing to slight differences in their respective densities, the recrystallizations can cause the permeability of the set cement to increase. At 250°C truscottite (C<sub>7</sub>S<sub>12</sub>H<sub>3</sub>) begins to appear. Owing to the manner in which truscottite crystallizes, a reduction in  
20 permeability is usually observed. (Nelson, Well Cementing - "Thermal Cements" 1990 9.1 – 9.19; J P Gallus et al, "Performance of Oil-Well Cementing Compositions in Geothermal Wells" SPE 7591 1978; L H Eilers et al, "High Temperature Cement Compositions – Pectolite, Scawtite, Truscottite or Xontolite: Which Do You Want?" JPT 1983 1373-1377).

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The degradation mechanisms described above are certainly not exhaustive, not least because the roles of other oxides present in the Portland cement, in particular alumina and ferrites, have been ignored, but they suffice to demonstrate the complexity of the phenomena occurring, without even considering the reaction products between the  
30 cement matrix and brines. In nature, in a geological medium, cement is thus meta-stable. In contact with brine, its mineralogical repertoire is modified by ion exchanges, which modify its physical qualities.

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The problems of cement disintegration when the temperature is raised are more severe when developing very deep wells, or injecting steam to recover highly viscous oils, or in geothermal wells to exploit geothermal energy. Geothermal wells are drilled into formations that contain superheated brines. At surface the brine is converted to steam which is then used to produce electricity. Steamflooding is a process where steam is injected into formations that contain viscous oil. The viscosity of the oil is reduced, allowing it to be pumped to surface. The temperature and pressure conditions encountered in these “thermal” wells vary between 200–300°C and 10 MPa – 95 MPa, respectively.

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An approach explored in work by Roy et al. (“Potential New High Temperature Cements for Geothermal Wells” AIME International Symposium on Oilfield and Geothermal Chemistry, Houston, TX 1979, pp 153-161) showed that the mineral anorthite was promising as a binder in geothermal well cements. However, the practical problem of formulating a pumpable cement slurry with a predictable working time remained to be solved.

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Other approaches to the problems of high temperature cements can be found in US 5,900,053; US 6,143,069; US 6,332, 921; US 6,367,556; WO 01/70646; and GB 0203729.9.

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The present invention resides in the recognition that rocks of basic compositions (poor in silicon, rich in calcium) maintain low porosity and a good mechanical resistance during weathering and can be considered as good natural analogues to conventional cements. Anorthite, grossular, prehnite and zeolite occur in basic rocks of magmatic origin, transformed in metamorphic or hydrothermal conditions.

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The object of this invention is to develop novel formulations suitable for cementing oil, gas, geothermal wells or the like, based on a Portland and alumina type cement tending to form mineral phases such that the properties of the cement matrix, in particular regarding compressive strength, do not degrade in practice under the effect of a rise in temperature and pressure (250°C-300°C; 20 MPa) and/or chemical attack (brines).

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The present invention provides a method of designing a cement slurry, comprising:  
determining a temperature to which the cement slurry will be exposed in situ;  
determining a stable, thermodynamic equilibrium composition of a CaO-Al<sub>2</sub>O<sub>3</sub>-  
5 SiO<sub>2</sub>-H<sub>2</sub>O (CASH) mineral system at the determined temperature; determining  
proportions of cement and mineral oxides required to provide a mixture having the  
determined composition of the CASH mineral system; and defining a series of  
particulate materials of predetermined particle sizes and densities, and comprising the  
cement and mineral oxides in the determined proportions such that, when mixed with  
10 water, a pumpable slurry is formed.

The proportions of cement and mineral oxides required to form a stable cement can be  
determined from general thermodynamic rules, phase relations between minerals and  
fluids and minerals, activity models and homogenous and heterogeneous phase  
15 equilibria known and developed for natural silicon- and calcium-rich rock systems of  
mafic origin to predict the mineralogy and chemical behaviour of Portland cements or  
derived compounds set in environments comparable to those encountered in  
geological settings such as hydrothermal fields of metamorphism (temperature greater  
than 150-200°C, pressure greater than liquid-vapour transition curve).

20 The method provides cement slurries that promote anorthite formation during the  
hydration of operating slurry by adding specific modifiers. Anorthite, characterized by  
solid solutions, exhibits the best adaptation to severe chemical environment.

25 In order to promote the formation of anorthite, specific modifiers have to be added to  
the cement powder. At the same time, the final slurry density often has to be as low as  
possible (e.g. 1.4 to 1.5 sg) (due to the low fracture gradients generally experienced in  
geothermal wells) while maximizing the solid fraction of the slurry to decrease the  
permeability and increase the compressive strength.

30 To achieve this, the physics of optimizing the packing between the different  
components of the material has to be mastered. The particle size distribution of each  
component has to be optimum. For example, the solid components can be provided in

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three distinct particle size fractions to optimize the amount of solids in the mixture.  
This technique allows the use of large amounts of solids while making the slurry still  
easily pumpable.

- 5 Class G cement can conveniently be used as the hydraulic binder. Cenospheres or  
other hollow particulate material of very low density (0.7 to 0.8 sg) can be added to  
decrease the slurry density. Silica flour and aluminum modifiers are the other  
components of the blends.
- 10 Apart from the cement for which the particle size is typically defined by the  
manufacturer, particle size of cenospheres, silica and aluminum modifiers are  
carefully selected in order to achieve maximum packing of the blend. The size and the  
crystallinity of the different blend components allow control of the kinetics of  
anorthite formation.

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The present invention will now be described by way of examples, with reference to  
the accompanying drawings, in which:

Fig. 1 shows a plot of blend compositions in the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  ternary diagram;

- Fig. 2 shows mineral phases known to be stable in natural calcium-rich systems  
plotted of in the  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  ternary diagram ( $\text{H}_2\text{O}$  in excess);

Figs. 3a and b show SEM microphotographs of set cement matrix obtained in a  
“xonotlite dominant” sample;

Figs. 4a and b show SEM microphotographs of set cement matrix obtained in an  
“anorthite dominant” sample; and

- 25 Figs. 5a and b show SEM microphotographs of a set cement matrix of a further  
sample.

Different cement blends are prepared according to the method of the invention. Table  
1 summarizes the physical properties of the blends and slurries. All slurry properties  
30 have been measured as per API specifications (API Recommended Practice for testing  
Oil-Well Cements and cement Additives (1990) API Spec.10 Fifth Edition  
(07.01.1990)). The compositions of blends in the quaternary system ( $\text{CaO-SiO}_2\text{-}$   
 $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$ ) are shown in Figure 1.

**Table 1: Properties of the slurries**

No slurry	#3	#4	#5	#2	#1
Density (g.cm <sup>-3</sup> )	1.4	1.49	1.49	1.94	1.89
W/C ratio	1.3	0.58	0.81	1.07	0.69
Solids Volume Fraction	0.40	0.59	0.59	0.43	0.42
Free Water	0	0	0	0	0
Blend	Cement Silica flour Cenospheres -	Cement Silica flour cenospheres Aluminum modifier	Cement Silica flour cenospheres Aluminum modifier	Cement Silica flour Silica Aluminum modifier	Cement Silica Flour - -
Plastic viscosity (cP)/Yield value after mixing (lbs/100 sqft)	33/6	257/29	109/9	53/21	149/11
Plastic viscosity (cP)/Yield value after 20 min conditioning (lbs/100 sqft)	16/13	109/3	54/6	30/15	85/7
Reading on FANN mod.35SA viscosimeter (R1-B1-F1) Gel at 10 min	11	21	15	35	4
Thickening Time (hours)	6:00	4:54	4:16	5:09	4:52
Transit Time	0:06	0:02	0:05	0:15	0:05
Compressive Strength after 24 hours at 400°F					
50 psi	3:43	4:40	4:34	6:02	-
500 psi	11:55	5:53	6:15	6:55	4:29
24:00	680	2100	1480	2420	6000

The slurries are mixed following the API procedure. Mixing is done in a Waring  
 5 Blender. All solid components are dry blended before being added to the water containing the liquid additives.

Once the slurry design has been optimized, samples are prepared for curing by  
 pouring the mixed slurry into a 5cm x 5cm x 5cm steel molds. Five cubes are  
 10 prepared for each formulation.

The molds containing the slurries are cured for three days at 300°C over 21 MPa in a standard oil well cement-curing chamber in water. The temperature is gradually increased to 300°C over a 6-8 hour heat up period, to minimize possible cracking of

( the samples due to thermal expansion. The temperature is maintained at 300°C and 21 MPa for 28 days, after which the system is allowed to cool down to room temperature.

- 5 The cured set cement samples obtained after 28 days exposure at 300°C, are drilled in 2.5 x 5 cm cores. These set samples are exposed to the production brine at 300°C over 21 MPa in the high pressure – high temperature geothermal reactor for 28 days. The brine is regularly changed (every 3 days) to keep the solution saturated and to simulate as close as possible actual well conditions, where the brine is an “open system”. The heating rate to reach 300°C is 6°C/min.
- 10

Samples are then removed, kept under water at room temperature before being tested for the following physical property measurements:

- 15 ☐ Uniaxial compressive strength performed on 2.5 x 5 cm cores in using a compressive machine  
☐ Water Permeability

- Mineralogical examination is carried out by x-ray powder diffraction using CuK $\alpha$  radiation. Scanning Electron Microscope images are used to describe morphologies of reaction products and to complete the XRD analysis.
- 20

- Two types of brines are used to simulate the chemical attack. Table 2 shows the chemical composition of a production brine circulated in a Japanese geothermal well at 1300 meters with a production temperature around 300°C. The pH of this brine is 2.6.
- 25

Table 2: Chemical composition of the production brine (Brine1)

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Ions	mg/l
Na	3120
K	810

Ca	1460
Mg	270
Cl	9570
SO <sub>4</sub>	201
SiO <sub>2</sub>	144
Fe	648

The table 3 shows the composition of a California brine.

5 Table 3:Chemical composition of the field brine (Brine 2)

Ions	g/l
NaCl	200
KCl	23
CaCl <sub>2</sub>	63
MgCl <sub>2</sub> .6H <sub>2</sub> O	1

The results of the mineralogical composition of the different samples before and after  
10 brine attack are presented in the following table.

Formulation Number	#3		#4		#5	#2		#1	
Density g/cm <sup>3</sup>	1.49		1.49		1.49	1.94		1.94	
Brine 1 or 2 attack at 300°C @28days	Before brine attack	After Brine 1 attack	Before brine attack	After Brine 1 attack	Before brine attack	Before brine attack	After Brine 2 attack	Before brine attack	After Brine 2 attack
Xonotlite C <sub>6</sub> S <sub>6</sub> H	+++ +	+++ +	++	++	++	++	++	+++ +	+++ +
Anorthite CaAl <sub>2</sub> Si <sub>2</sub> O <sub>8</sub>	++	++	+++ +	-	++++	+++	+++ +	-	-
Anorthite,sodium,intermediate (Ca,Na)(Si,Al) <sub>4</sub> O <sub>8</sub>	-	-	-	+++ +	-	-	++	-	-

Albite $\text{NaAlSi}_3\text{O}_8$	-	-	-	+++	-	-	-	-	-
Wairakite $\text{CaAl}_2\text{Si}_9\text{O}_{12} \cdot 2\text{H}_2\text{O}$	-	-	++	++	++	-	-	-	-
Prehnite (zeolithe) $[\text{Si}_3\text{AlO}_{10}]\text{Ca}_2\text{Al}(\text{OH})_2$	-	-	-	-	-	++	+	-	-
Epidote 1-2 $[\text{Si}_2\text{O}_7][\text{SiO}_4](\text{OH})\text{Al}_2\text{OCaAl}_2$	-	-	-	-	-	++	++	-	-
Garnet $[\text{SiO}_4]_3\text{Al}_2\text{Ca}_1$	-	-	-	-	-	-	++	-	-
Quartz $\text{SiO}_2$	+	-	-	-	+	+++	-	-	-
Corundum $\mu\text{Al}_2\text{O}_3$	+	-	+	-	++	++	-	-	-

++++ Prevailing phase; +++ phase in appreciable amount; ++ phase in fairly good amount; + phase in small amount.

- 5 Figure 2 presents in the same quaternary system CASH as shown in Figure 2, the blend compositions from Table 1 and the different mineral phases of basic rock after hydrothermal alteration known as stable at 300°C.

Two areas can be defined:

- 10
- Area 1, outside the two joins Epidote-pectolite and Prehnite-pectolite
  - Area 2 near or inside these two joins where the formation of xonotlite can be avoided or limited.

- 15 In area 1, two compositions have been tested, #1 and #3 with 1.94 and 1.49 g/cm<sup>3</sup> densities respectively. The phase responsible for the cementing properties within this region is mainly xonotlite.

With the low-density cement composition (#3), anorthite in a fairly good amount is easily detected. Its composition contains more alumina than the one at higher density.

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After brine 1 attack, the set cement matrix shows deleterious signs and the water permeability after one month in the Brine 1 increases. Fine needles of xonotlite shows dissolution signs particularly on the core borders.

5 In area 2, the compositions #4, #5, #2 are investigated. The composition #2 has a density of  $1.94 \text{ g/cm}^3$  and is cured in the brine 2. Compositions #4 and #5 have a lower density,  $1.49 \text{ g/cm}^3$ . Phases responsible for the cementing properties within this area are mainly anorthite, whatever the slurry density. For the composition # 4, a high temperature calcium zeolite, wairakite well detected by XRD and SEM analysis  
10 contributes with anorthite to favourable cementitious properties at  $300^\circ\text{C}$ . The composition #5, containing more alumina and less silica but having the same density, shows a mineralogical “assemblage” more complex: relic phases as silica and alumina are well detected and wairakite is less observed with SEM. This composition seems to be slower than #4.

15 If the slurry density is initially higher (#2), anorthite stays the main binder but prehnite, epidote are well detected. Relic phase as silica and alumina are still not completely consumed after one month at  $300^\circ\text{C}$ . Wairakite is not detected. Composition #2 contains a part of silica coarser than the one added in the composition  
20 #5. That can explain a lower reactivity after one month resulting from lower water saturation in silica useful to form this phase.

After brine attack, whatever the slurry density, anorthite evolves to a sodic plagioclase member, albite that shows well the good adaptation of anorthite to  
25 chemical alteration.

The compressive strength and the water permeability of the set cement after curing without or with the brine are presented in table 5.

30 Table 5: Compressive strength before and after brine attack and water permeability after brine attack for the different compositions.

Formulation Number	#3	#4	#5	#2	#1
Density g/cm <sup>3</sup>	1.49	1.49	1.49	1.94	1.94
BHST°F	300	300	300	300	300
Compressive Strength (psi) at BHST after 1 month	900	2332	800	2207	6352
Water permeability (mD)	0.66	0.16	0.2	-	-
Compressive Strength (psi) at BHST after 1 month in brine	830	2500	-	2300	5400
Water permeability (mD) after brine attack	2.81	0.26	-	-	-

- Even though the value of the compressive strength is lower for blend #2 than #1 before brine attack, after brine attack, the formulation #2 shows no decrease in the compressive strength. If the brine is directly added as mixing water, this trend is still observed contrary to the trend obtained with the formulation #1 where the compressive strength decrease of 55% of its initial value.

The formulation #4, at a density of 1.49 shows no variations in the compressive strength before and after brine attack and only a slight increase in permeability.

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The composition #5 exhibits the lower compressive strength with a chemical system not completely reacted.

- Electron microscopy gives morphological information that completes the chemical, physical, mechanical and diffractometric data. The set cement matrices provided from formulation #3 and formulation #4 are observed and compared before and after chemical attack. Figures 3a and b, and 4a and b present the set cement matrix obtained with the composition #4. Anorthite is well detected before and after brine attack in the interstitial matrix and crystallizes as interlocking platelets, which can contribute to a superior compressive strength measurement (Figures 3a and b). This phase is also met in some cavities observed in this low-density system. Again anorthite crystallizes under interlocking platelets, plugging the cavity (Figure



( 4a). Wairakite is well observed in the interstitial matrix under cubic crystals and seems well stable after brine curing (Figure 4b).

Figures 5a and b present the set cement matrix obtained with the composition #3. The samples have been cut in the core near the free surface and inside the core. In view of XRD analysis, xonotlite as fine needles, is the primordial hydrate. Figures 5a and b show the effect of brine curing through the core: in the core near the free surface, the signs of xonotlite dissolution in the interstitial matrix are more significant than inside the core. In view of the SEM observations, the increase of water permeability after brine curing can be explained: 0.66 mD and 2.8 mD before and after brine attack, respectively.

In view of the mechanical and durability results, the composition #4 seems to be the best candidate for geothermal applications. The permeability and the compressive strength are not affected after brine attack at 300°C. Indeed, the results have shown that the faster anorthite forms the lower strength retrogression is observed: at 300°C, the composition #4 exhibits the higher compressive strength with a complete reaction after one month at high temperature, the composition #5 exhibits the lower compressive strength with a chemical system not completely reacted.

The fact that the original material component (cement, cenosphere, aluminum modifiers) have completely reacted can partially explain this durability. Indeed, unreacted silica, and aluminum modifiers react with brine to give secondary phases which are not necessarily stable under these conditions.

Anorthite is the calcic member of the solid solution plagioclase that is well known to be stable at high temperature and which can adapt to brine circulation by ions exchanges in its network. Wairakite is a high temperature Ca-zeolite that is able, like all zeolite, to absorb ions in its structure that can be a good property with brine circulation. Its stability domain is well known in the system  $\text{Na}_2\text{O}-\text{CaO}-\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{H}_2\text{O}$  in the range 0-500°C and 01-10kbar involving the phase's anorthite, grossular, prehnite and others. This phase does not exist in formulation #2 at higher density. A fraction of the silica in Composition #2 is coarser (silica) than the silica

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contained in Composition #5 (silica flower). That can explain a lower reactivity after one month resulting from lower water saturation in silica useful to form this phase. This also shows how the kinetics of the targeted phases (anorthite, wairakite) could be controlled by the particle sizes of the different components of the blend.

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The present invention provides lightweight formulation using conventional Class G cement for temperatures up to 300°C. The set cement can show very good indications of durability (low permeability and no strength retrogression).

- 10 In the process used to design the slurry, the temperature stable phases (anorthite, wairakite) are selected; aluminum modifiers and silica oxides are added to the dry cement so that the elemental composition of the blend corresponds to the phases selected; the control of the particle size distribution and the relative amount of those minerals allow their addition at high concentration while leaving the slurry easily  
15 mixable and pumpable; and the kinetics of the targeted phases formation is then controlled by adjusting the crystallinity and the particle sizes of the different solids.

- The methods of the invention can be used to design cement blends of a suitable cement and other solid additives which, when mixed with sufficient water can form  
20 pumpable slurries. In well cementing, the slurries are pumped into the well in question and allowed to set to provide zonal isolation and well stabilization. The compositions can also be used to line pipes. In this case, a cement slurry is placed inside a pipe, which is then rotated, typically at high speed to coat the slurry onto the inside of the pipe where it is allowed to set.

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CLAIMS

- 1 A method of designing a cement slurry, comprising:
- 5 i) determining a temperature to which the cement slurry will be exposed in situ;
- ii) determining a stable, thermodynamic equilibrium composition of a mineral system, analogous to the cement when set, at the determined temperature;
- 10 iii) determining proportions of cement and mineral oxides required to provide a mixture having the determined composition of the mineral system; and
- iv) defining a series of particulate materials of predetermined particle sizes and densities, and comprising the cement and mineral oxides in the determined proportions such that, when mixed with water, a pumpable
- 15 slurry is formed.
- 2 A method as claimed in claim 1, wherein the mineral system is a  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  (CASH) mineral system.
- 20 3 A method as claimed in claim 1 or 2, wherein the cement is a Portland or alumina type cement.
- 4 A method as claimed in any of claims 1 – 3, wherein the series of particulate materials is defined so as to promote the formation of anorthite.
- 25 5 A method as claimed in any preceding claim, wherein the series of particulate materials is selected to provide a pumpable slurry of density less than 1.94.
- 6 A method as claimed in claim 5, wherein the step of defining the series of
- 30 particulate materials includes selecting a low density particulate component having a density of less than 0.8 sg as part of the series.

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- 7      A method as claimed in any preceding claim, wherein the step of defining a series of particulate materials includes the step of defining a series of discrete particle size fractions to optimise the packing of the solid particles in the slurry.
- 5      8      A cement blend comprising a series of particulate materials, including cement, defined in accordance with the method of any preceding claim.
- 9      A cement slurry, comprising a cement blend as claimed in claim 8 mixed with sufficient water to form a pumpable slurry.
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- 10      A method of cementing a high temperature well, comprising:
- 15      i)      designing a cement slurry according to a method as claimed in any of claimed 1 – 8 such that the temperature of the well is used as the determined temperature;
- 15      ii)     forming a slurry from the defined series of particulate materials and water; and
- 15      iii)    pumping the slurry into the well.
- 11      A method of lining a pipe for high temperature fluids, comprising:
- 20      i)      preparing a cement slurry as claimed in claim 9, the determined temperature being the temperature of the fluids in the pipe;
- 20      ii)     placing the slurry in the pipe; and
- 20      iii)    rotating the pipe so as to deposit the slurry evenly on the inner surface of the walls of the pipe.

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Application No: GB 0213690.1  
Claims searched: 1-11

Examiner: Kathryn Orme  
Date of search: 30 October 2002

## Patents Act 1977 Search Report under Section 17

### Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:  
UK Cl (Ed.T): C1H (HCH)  
Int Cl (Ed.7): C04B  
Other: Online: WPI, EPODOC, PAJ

### Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	WO 01/70646 A1 (SCHLUMBERGER) see especially page 1 lines 5-6 and 18, page 2 lines 22-27, page 3 lines 7-18 and page 6 and Table 3	1-10
X	WO 97/49644 A1 (NOWSCO WELL SERVICE) see especially page 3 lines 19-20, page 4 lines 1-5 and 26-28, page 7 lines 8-10 and 35-36	1-10
X	US 6332921 B1 (BROTHERS ET AL) see especially col 2 lines 31-37, 62 and 67, col 3 lines 19-21 and 37-39, col 4 lines 15-16	1,5,6 & 8-10
X	US 5158613 (SARGEANT ET AL) see especially col 2 lines 6-8, col 3 lines 44-55, col 4 lines 29-32	1-3,5 & 8-10
X	US 4935060 (DINGSOYR) see especially col 1 lines 56-67, col 2 lines 5-11, col 3 lines 36-46	1-3 & 8-10
X	US 4877452 (ROUSSEL ET AL) see especially col 1 lines 7-10, col 3 lines 6-30 and 66-68 and col 4 lines 1-9 and 59-64	1-3 & 8-10

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X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application